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"Synthesis and Structural Characterization of Pt-Si Dimers
with Unusually Short Cross-Ring Silicon-Silicon Interactions"

by

Eugene A. Zarate, Claire A. Tessier-Youngs, and Wiley J. Youngs

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Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106

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Synthesis and Structural Characterization of Pt-Si Dimers with Unusually Short Cross-Ring Silicon-Silicon Interactions

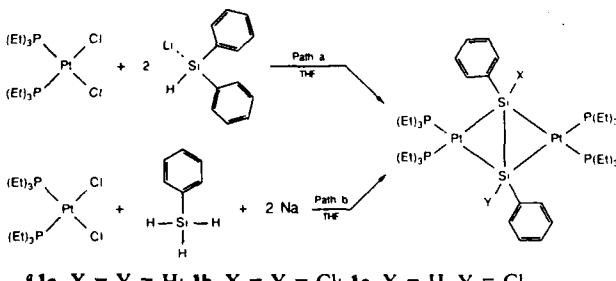
Eugene A. Zarate, Claire A. Tessier-Youngs,* and Wiley J. Youngs*

Department of Chemistry
 Case Western Reserve University
 Cleveland, Ohio 44106

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Polysilanes have use in applications where photosensitivity is required and as precursors to β -SiC.¹ Polysilanes are usually prepared from dichloroorganosilanes and sodium at $\approx 100^\circ\text{C}$.² Several reports of transition-metal-catalyzed formation of polysilanes from R_2SiH_2 and RSiH_3 have appeared in which product distributions have been the main focus.³ The mechanism of this

Scheme I^a



catalytic process is poorly understood.^{2b-d,3} Dimeric silyl- or hydride-bridged complexes of titanium and zirconium are the only reported metal-containing species isolated from catalytic silane polymerizations.⁴ Herein we report the synthesis and structural characterization of a series of platinum-silyl dimers with unusually short cross-ring Si-Si distances. These dimers are catalysts or catalyst precursors in silane oligomerization reactions.

The preparation of cocrystallized mixtures of three platinum-silyl dimers $[(\text{EtI})_3\text{P}-\text{Pt}(\text{SiPhX})(\text{SiPhY})-\text{Pt}(\text{PEt}_3)_2]$ (**1a**, X = Y = H; **1b**, X = Y = Cl; and **1c**, X = H and Y = Cl) from two very different reaction paths is shown in Scheme I. The reaction of $\text{PtCl}_2(\text{PEt}_3)_2$ ⁵ with LiSiHPh_2 in THF (path a, Scheme I) yields a small quantity of the cocrystallized mixture **1a-c** as air stable yellow crystals suitable for X-ray diffraction studies. The complexes **1a-c** are the major platinum-containing products produced by the reaction of $\text{PtCl}_2(\text{PEt}_3)_2$ with SiH_3Ph in THF with the addition of a slight excess of sodium powder (path b, Scheme I).⁷

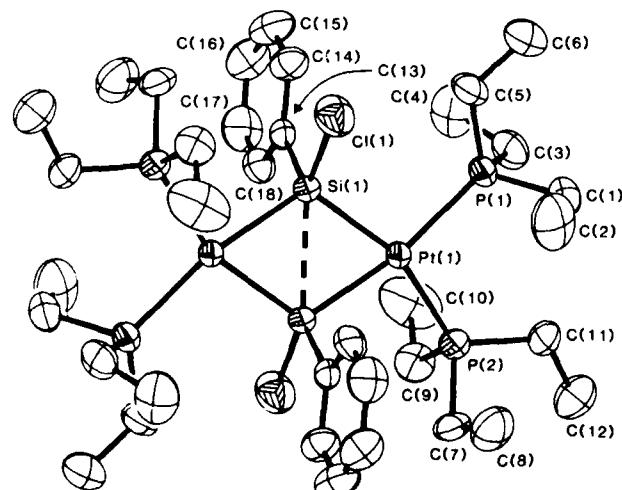


Figure 1. ORTEP labeling diagram of **1a-c** and **1b**. The thermal ellipsoids are drawn at the 20% probability level. Hydrogens are omitted for clarity.

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(5) $\text{PtCl}_2(\text{PEt}_3)_2$ was prepared from $\text{PtCl}_2(\text{NC-Ph})_2$ and PEt_3 . Its properties were as reported by Jensen (Jensen, K. A. Z. *Anorg. Allg. Chem.* 1936, 229, 225-281).

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(7) All reactions were conducted under an argon atmosphere. The product from path a was obtained by removing the THF under vacuum followed by extraction with and recrystallization from hexane. The reaction mixture of path b showed the evolution of gas, presumably H_2 . Filtration of the mixture and removal of the solvent leaves a dark brown oil which when quickly washed with acetone yields the yellow solid **1a-c**. Low isolated yields (10-20%) of pure **1a-c** from path b are due to reaction of acetone with **1a-c** and to difficulties in completely removing traces of the liquid oligomeric silanes from **1a-c** via subsequent recrystallizations from hexane.

Crystals of pure **1b** can be obtained by treating toluene solutions of **1a–c** with carbon dioxide followed by recrystallization from benzene. Apparently the Si–H bonds of **1a** and **1c** react with carbon dioxide to yield unidentified complexes, whereas **1b** is unreactive.

Both paths a and b in Scheme I are complicated by partial chlorination of the Si–H bonds. This is not unexpected because Noble metals catalyze chlorination of Si–H bonds using a variety of chloride sources.⁸ Path a proceeds with the net loss of a phenyl substituent. We have not determined whether this can be attributed to a metal-catalyzed disproportionation of the substituents^{2,4,3,9,10} or to rearrangement of the silyllithium reagent.¹¹

The addition of catalytic quantities of **1a–c** to phenylsilane yields di- and trisilanes, with some scrambling of the phenyl and hydride substituents.¹² The di- and trisilanes are also produced by the addition of $\text{PtCl}_2(\text{PEt}_3)_2$ to excess SiH_3Ph and are byproducts of path b.¹²

Field desorption mass spectrometry of **1a–c** clearly shows that all three dimers are present in the crystalline compound. The X-ray study of the product from path a was performed.¹³ Alternating refinements to convergence holding the thermal parameters of the chlorine atom fixed while the occupancy factor was freed and vice versa shows that a silyl chloride is present in place of a silyl hydride approximately 65% of the time in this particular crystalline mixture.¹³ Pure **1b** has also been crystallographically characterized.¹⁴ All products were further characterized by IR and NMR spectroscopy.^{15,16}

An ORTEP drawing of the structure of **1a–c** and pure **1b** is shown in Figure 1. The silicon atoms and H or Cl and phenyl substituents lie in a plane which is perpendicular to the Pt–Pt vector and the plane defined by the platinum–silicon ring. The Si–Si separations in **1a–c** (2.575 (15)–2.602 (4) Å) are within the range of known single Si–Si bonds (2.33–2.70 Å)¹⁷ and are the shortest cross-ring Si–Si distances in any metal–silicon four-membered ring.^{18–20} The Pt–Si bonds (2.355 (7)–2.383 (8) Å) are long when compared to other Pt–Si bonds in environments of similar steric demands.^{10,18} The acute deviation of the angle at the “square-planar” platinum atoms (Si–Pt–Si = 65.9 (3)–66.5 (1)°) and the increase in the angles of the “tetrahedral” silicon atoms (Pt–Si–Pt = 113.6 (1)–114.2 (3)°) suggest that the Si–Si interaction forms

an integral part of the bonding scheme. The acute Si–Pt–Si angle is not a result of van der Waals repulsions between the platinum atoms because the Pt–Pt distances range from 3.973 (1)–3.997 (2) Å, whereas platinum has a van der Waals radius of 1.7–1.8 Å.²² The large cross-ring Si–Si separations (3.852–4.225 Å),²¹ acute M–Si–M angles (69.6–75.0°), and short M–M distances (2.708–3.183 Å) of most other metal–silicon dimers are in sharp contrast to those of **1a–c**.^{10,18–20} Only $[\text{Cp}_2\text{TiSiH}_2]_2$ has a similar cross-ring Si–Si distance (2.69 Å)²⁰ and M–Si–M angle (103°).²⁰

The π -coordination of the disilene $\text{PhXSi}=\text{SiYPh}$ to two $\text{Pt}(\text{PEt}_3)_2$ moieties provides a bonding picture of the complexes **1a–c** which is consistent with their geometry. This bonding picture of **1a–c** has been supported by a recent theoretical investigation.²³ The π -coordination of a bulky disilene to a single platinum has been reported, but crystallographic data are not available.²⁴ As a consequence of π -coordination, the Si–Si distance of **1a–c** is lengthened by 19–22% from that in free disilenes (2.13–2.16 Å).²⁵ This percent lengthening can be compared to the 12% or 27% lengthening of the C–C distance in $\text{CH}_2=\text{CH}_2$ on π -coordination to two zirconium centers in $\text{Zr}_2\text{X}_6(\text{PEt}_3)_4(\text{CH}_2=\text{CH}_2)$ (X = Br or Cl, respectively).²⁶ In **1a–c** and $\text{Zr}_2\text{X}_6(\text{PEt}_3)_4(\text{CH}_2\text{CH}_2)$ the resultant Si–Si (2.58–2.60 Å) or C–C (1.56 and 1.69 Å) separations are longer than the “typical” single bond distances (Si–Si = 2.34 Å and C–C = 1.54 Å).²² The bonding descriptions of **1a–c** and the zirconium–ethylene complexes²⁶ are extensions of the Dewar–Chatt–Duncanson (DCD) model, which recently has also been applied to the cross-ring Si–Si interactions in $[\text{R}_2\text{SiX}]_2$ (X = CH_2 , NH, O, PH, or S).²⁷ The chemistry of **1a–c** shows similarities to that of π -coordinated diphosphene complexes because the synthesis of $\text{M}(\eta^2\text{RP}=\text{PR})\text{L}_n$ can involve monophosphorus reagents^{28,29} and similar DCD bonding schemes have been developed.²⁹ As a consequence of the bonding scheme the silicon of **1a–c** are pentacoordinate in a highly distorted trigonal bipyramidal geometry.^{30,31} Placing the platinum atoms in the axial positions is consistent with the relatively long Pt–Si bonds,³⁰ and this results in positioning the hydrides in their favored

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(12) Determined by FD-MS, IR, and NMR data.

(13) (a) Crystallographic data for **1a–c**: space group, $P2_1/n$; $a = 10.985$ (2) Å, $b = 11.803$ (2) Å, $c = 17.636$ (3) Å, $\beta = 99.62$ (2)°, $V = 2254.4$ (8) Å³, and $Z = 2$. Intensity data were collected from $3.0 < 2\theta < 50.0^\circ$. Refinement on the basis of 1946 reflections ($I \geq 3\sigma$) resulted in a final $R = 0.068$ and $R_w = 0.070$. (b) UCLA Crystallographic Computing Package, December 2, 1985. Numerical absorption correction was applied.

(14) Crystallographic data for **1b**: space group $P2_1/n$; $a = 10.962$ (2) Å, $b = 11.833$ (2) Å, $c = 17.609$ (4) Å, $\beta = 99.62$ (2)°, $V = 2252.2$ (8) Å³, and $Z = 2$. Intensity data were collected from $3.0 < 2\theta < 52.0^\circ$. Refinement on the basis of 4116 reflections ($I \geq 3\sigma$) resulted in a final $R = 0.054$ and $R_w = 0.043$. See ref 13b.

(15) Selected spectral data for the mixture **1a–c**: IR (Nujol mull) $\nu_{\text{Si–H}} = 1955$ (m) and 1980 (m) cm⁻¹; ^1H NMR (C_6D_6) 0.85 (m, CH_3), 1.72–1.83 (m, CH_2), 4.37 (m, SiH); 7.25, 7.71, and 7.94 (t, d, and d, respectively, C_6H_5). Except for the absence of the Si–H signals, the IR and NMR data for **1b** are virtually identical with those of **1a–c**.

(16) Hydride bridges on the metal–silicon bonds are a common feature in the structures of metal–silicon four-membered rings.¹⁰ We find no evidence of such in the crystallographic or spectra data of **1a–c** or **1b**.

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equatorial sites.³² The inclusion of the Si-Si bond in two fused three-membered rings can help explain its length.³³

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Registry No. 1a, 113999-66-9; 1b, 113999-67-0; 1c, 113999-68-1; PtCl₂(PEt₃)₂, 15390-95-1; LiSiHPh₂, 17950-77-5; PhSiH₃, 694-53-1.

Supplementary Material Available: Tables of data collection and refinement details, atomic positional parameters, thermal parameters, and bond lengths and angles for the cocrystallized dimers 1a-c and dichloride dimer 1b (10 pages); observed and calculated structure factors for 1a-c and 1b (27 pages). Ordering information is given on any current masthead page.

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